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The explanation of the causes of pore formation in deposits is one of the most important problems in the electrolytic deposition of metals. Usually the term "pores" refers to macro -- and micro -- canals running from the surface of the deposit to the basic metal of the cathode. In metal deposits obtained by electrolytic methods the pores may be of vastly different sizes. This fact greatly hinders the determination of their number and size. One may either detect or not detect pores in the same planting, depending on the conditions and the duration of the tests. Consequently a deposit may appear non-porous when specimens, covered by a protective plate of a given thickness, are tested in liquid media, and porous, when tested in an atmosphere of active gases. Thus, evaluation of the porosity of a deposit is relative.

One may divide pores arbitrarily into two groups according to their size:

(1) Large pores forming mainly as a result of the heterogeneity of the electrode surface. This heterogeneity may be caused by various types of inclusions -- non-metallic, heterogeneous metals, oxides, surface tension lowering substances, etc.

(2) Small pores formed by the structure of the electrolytic deposit (shape, size and distribution of the crystals), which depends

on the electrolysis conditions.

The difficulty in studying the porosity of electrolytic deposits is basically connected with the absence of a precise quantitative method of discovering pores. Applying the quantitative method to the study of porosity is complicated by the fact that pores can be of most varied shapes and sizes.

There are relatively few works dealing with the study of porosity and generally they are only incidental to the study of various individual problems of the electrolytic deposition of metals.

This work deals with the influence of certain factors on the porosity of electrolytic deposits of nickel.

EXPERIMENTAL PART

The electrolytic deposition of nickel was mainly conducted in a bath of the following composition (in grams per liter:) $NiSO_4 \cdot 7H_2O$ -- 166; H_3BO_3 -- 30; $Na_2SO_4 \cdot 10H_2O$ -- 50; $MgSO_4 \cdot 7H_2O$ -- 20, and Nacl -- 2.

The electrolysis was conducted in closed glass containers. The volumes of the electrolyte was 0.5 liters. Chemically pure nickel served as the anode, while iron plates with a surface of 2 square centimeters served as the catode. The experiments were carried out at a temperature of 17 -- 20 degrees centigrade.

Method of Exposing Pores

The commonly employed reagent with potassium ferrocyanide of the following composition (in grams per liter): $K_3Fe(CN)_6$ -- 10, and Nacl -- 20, was used for exposing pores on an electrolytic deposit of nickel on iron specimens.

In this method, the reagent penetrates through the pores of the plating to the basic metal and reacts with it: the products of this reaction (Turnbull's salt) come back through the pores, and form blue spots on the surface. It is assumed that the number of pores is equal to the number of blue spots.

In the present work the porosity was determined as follows.

The specimens being tested was immersed for two minutes in a solution of reagent with potassium ferrocyanide as indicated above, after which it was washed in distilled water and dried with filter paper. The number of pores was counted under a microscope having a 50 fold magnification. In order to facilitate counting the total number of pores the surface of the specimen was divided into separate square sections. This made possible an accurate count. Counting the pores under the microscope allowed exposure of a large number of small pores which could not be seen with the naked eye.

Effect of the Lining and Preliminary Processing on Porosity.

Preliminary conditioning of the cathode surface was a substantial effect on the porosity of the electrolytic deposit (1--3), We studied the effect of various kinds of preliminary processing of the cathode on the porosity of the electrolytic deposits of nickel. The deposits obtained on a cathode previously polished by emery paper of various grades produce a different number of pores. The rougher the finish of the electrode surface, the larger the number of pores in the deposit. The number of pores in the deposit decreases as the surface of the cathode is smoothed out.

After mechanical processing with emery paper No 120, the specimens were subjected to various chemical treatments: degreasing in a 10 percent solution of NaOH, electrochemical degreasing in a 10 percent solution of NaOH, degreasing in a 20 percent solution of Na_2CO_3 at a temperature of 80 degrees centigrade, mechanical rubbing of wet specimen with sodium carbonate and subsequent cleansing in acid solutions.

The best results were obtained after rubbing wet specimens with sodium carbonate. Apparently, in this case, the various heterogeneous particles which cling to the surface after mechanical processing, are eliminated more effectively. Consequently, the number of pores diminished sharply.

On the basis of the experiments which determined the effect of previous treatment on the number of pores in the electrolytic deposit "Standard" conditions were chosen for the preparation of the cathode. These consisted of the following: the specimens were polished with No 120 emery paper, washed with water, degreased by rubbing with sodium carbonate to complete wetness and were rewashed with distilled water. The deposition of nickel was effected on specimens thus prepared. As was indicated above, if the metal to be plated is heterogeneous, i.e., contains various inclusions, then the number of pores in the deposit grows sharply. For example, non-metallic inclusions which appear on the surface of the cathode as the result of its mechanical treatment, heterogeneous metals (admixtures), traces of grease and of surface tension lowering substances remaining after a faulty degreasing of the electrode, scales, etc., lead to the formation of porous deposits.

Of all the impurities, metallic impurities with a lowered hydrogen supertension produce the sharpest effect on porosity. In the electrolytic process the sections of the cathode with a lowered hydrogen supertension are at the same time the sections with an increased supertension for the deposited metal [4]. Therefore an intensive liberation of hydrogen occurs in these sections and the deposition of metal is sharply hindered. The intensive liberation of hydrogen in these sections of the cathode leads to the formation of crater-like depressions in the center of which are canals running to the basic metal. The constant flow of hydrogen bubbles leaves a noticeable trace in the form of a groove in the surface of the cathode.

If a cross section of the specimen is made at the points where such a crater-like depression was formed, and if a metallographic microsection is prepared it becomes evident that the large pores in the deposit are actually formed directly at the occlusion points. Next to the large pore many smaller ones are formed.

It must be noted that pores may form not only in the sections with a lowered hydrogen supertension, but also in the sections that were poorly degreased and in poor contact with the electrolyte.

In a number of works [5] it was shown that the firmness of adhesion and the size of the hydrogen bubbles at the moment of their liberation are related to the ratio of the surface tension on the border solution -- gas, solution -- metal and metal -- gas, i. e., are related to the marginal angle. The marginal angle changes sharply in relation to the presence of surface tension lowering substances in the electrolyte.

In the absence of impurities the value of the marginal angle is related to the potential of the electrode. With a change in polarization the marginal angle curve (ϑ) -- electrode potential (φ) passes through a maximum [6].

Thus the duration of the bubbles will change both with the change in concentration of the surface tension lowering substances and with the change of current density on the cathode. On the sections of the cathode where the adhesion of the hydrogen bubbles occurs, the deposition of the metal is hindered for a prolonged time [7], and as a result pores are formed.

Effect of the Plating Thickness on Porosity

It is obvious that, given an equal quantity of deposited metal, the degree of filling of the electrode surface with crystals will vary in relation to the size of the crystals. If the crystals are large, only a small portion of the electrode surface will be covered by a deposit, while with an equal quantity of deposited metal with minute crystals, the whole surface will be evenly covered by the deposit.

In order to cover the whole surface of the cathode with the depositing metal (large size crystals) to obtain a non--porous deposit it will be necessary to obtain from the electrolyte a considerably larger amount of metal than in the case of minute crystal deposition. Thus, for every given size of the crystals there must be a certain minimum quantity of metal which fills the whole surface. Such a quantity may be called "critical". Since the average thickness of the deposit is proportional to the quantity of the metal deposited on the cathode, the "critical" thickness guaranteeing non-porosity will vary in relation to the size of the crystals.

Consequently, with an increase in crystal size, the minimum thicknesses necessary for obtaining a non-porous deposit, must be increased.

If a curve is drawn of the ratio between the number of pores and the thickness of the plating for the various sizes of crystals, this curve will have a sharp bend in the case of oriented and tightly adhering crystals. This bend will indicate a complete covering of a given surface by crystals and the formation of a non-porous plating.

In order to obtain a non-porous deposit with low plating thicknesses it is necessary to choose electrolytic conditions under which regular, compact deposits with minute crystals are obtained.

Under practical electrolytic conditions, more often than not, the crystals are arranged in a disorderly fashion and it is natural that the relation between the size of the crystal and the minimum thickness will be more complicated and the bend of the curve (number of pores -- deposit thickness) will be more obtuse. In the case of disorderly arranged crystals, the minimum thicknesses guaranteeing a non-porous plating will be considerably higher than in the case of crystals tightly placed one next to the other.

[See Figure 1 on next page]

Figure 1 shows the results of studies of the relation between porosity and the thickness of nickel plating (5 -- 55). The electrolytic deposition of nickel was made on iron specimens treated under normal experimental conditions in solutions as indicated above, with a current density of 2 A/dm^2 and a temperature of 17-20 degrees centigrade. To draw the porosity -- plating thickness curve the

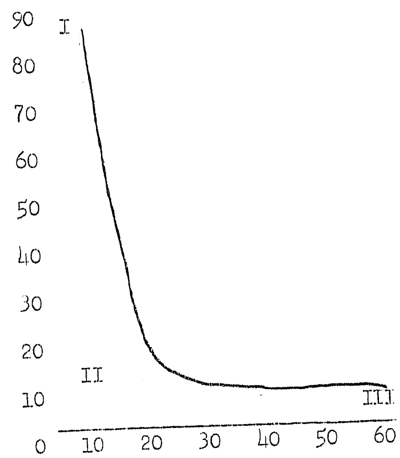

Figure 1

Relation between the number of pores and the thickness of the nickel plating. A - Number of pores; B - Thickness of plating (in μ).

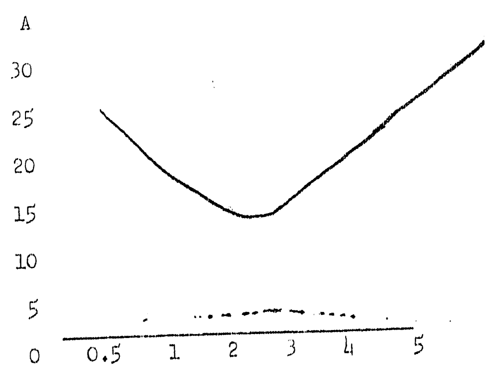

Figure 2

Relations between the number of pores forming in a nickel plating and the current density on the cathode. A - Number of pores; B - Current density (in amperes/decimeter).

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average plating thickness were used which were calculated from the total increase in weight in relation to the total surface of the electrode. From Figure 2 it is evident that with an increase of thickness, the number of pores decreases sharply up to a thickness of 15--17 μ , after which the curve bends. The number of pores changes little with a subsequent increase of thickness. (While studying the relation between the number of pores and the thickness of the nickel deposition specimens of different types of iron, the absolute values of the number of pores vary somewhat. However, the ratio remains the same.)

It is impossible to obtain an entirely non-porous deposit by increasing the thickness as high as 55 μ . In sector I-II a large number of pores is caused by the fact that the thickness of the plating does not reach the "critical" value while sector II-III the presence of the pores in the deposit is caused by the heterogeneity of the basic metal of the cathode.

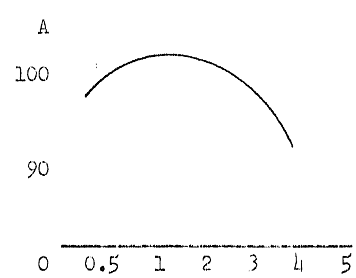

Figure 3

Output of current during deposition of nickel from a solution without admixtures, in relation to the current density. A - Output of current in (percentage); B - Current density in (amperes per square decimeter).

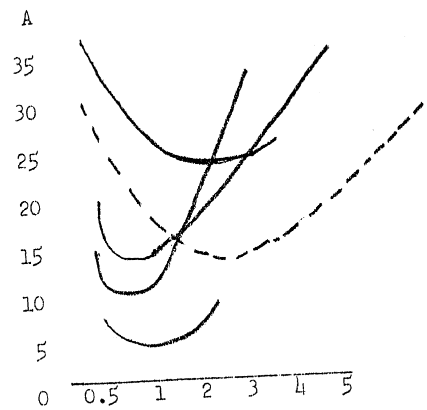

Figure 4

Relation between the number of pores formed in a nickel deposit and the current density of the cathode for various admixtures of surfaces tension lowering substances. A - Number of pores; B- current density (in amperes/square decimeter). Admixtures to the electrolyte with the composition mentioned above: 1 - 0.15 g/l of cresylic acid; 2 - 8 cm^3/l of formaldehyde; 3 - 8 cm^3/l of acetone; 4 - No admixtures; 5 - 3 g/l of 2, 6 -- and 2,7 -- disulfononaphtalinic acid (the composition of the electrolyte in this experiment, in g/l, was: $NiSO_4 \cdot 7H_2O$ -- 210; H_3BO_3 -- NaCl -- 3; NaF -- 6. This composition was suggested by Kudryavtsev [10].)

Effect of Current Density on the Porosity of an Electrolytic Nickel Deposit

Figure 2 shows the curve of the relation between the number of pores forming in a nickel plating and the current density. The deposits were obtained on iron specimens processed under normal conditions. The plating thickness was 17--20 μ .(A change of thickness between 17 and 20 μ (Figure 1) is hardly reflected in the number of pores.

As is evident from Figure 2, in relation to the current density, the number of pores passes through a minimum. The lowest number of pores (with the composition and temperature of the electrolyte indicated above) occurs with a current density of 2 amperes/square decimeter. The passage through the minimum of the relation between the number of pores in the deposit and the density of the current may be presented in the following manner.

A compact and uniform metal deposit is obtained within definite intervals of current densities. The large number of pores, which occurs in the electrolytic deposit of nickel with low current densities, may be caused by the following:

(1) If the deposition speed of the nickel crystals is lower than the passivation speed, then the growing crystals are rapidly passivated, their growth stops [8], the cohesion between the crystals is lowered, and the deposit comes out not compact and porous.

(2) With low current densities the deposition of the metal occurs mainly on the most active sections of the surface because of a comparatively low polarization of the cathode. Consequently, the deposition of the metal occurs mainly on the most active sections of the surface because of a comparatively low polarization of the cathode.

As a result of this the deposition of metal does not occur uniformly, but rather on separate sections of the cathode surface. With an increase of the current density, the deposition of metal occurs on less active sections as well [9]. With certain values of current density the deposit becomes more compact and uniform, and consequently the number of pores is at the minimum.

With a further increase of current density the number of pores in the deposit is increased by an intensive separation of hydrogen. This was controlled by means of the yield of nickel from the current. (Figure 3).

Effect of Surface Tension Lowering Substances on the Porosity of the Electrolytic Deposits of Nickel

The effect of various surface tension lowering substances on the porosity of the nickel deposit (acetone, formaldehyde, n -- cresylic acid, 2, 6 -- and 2, 7 -- disulfononaphtalinic acid and others).

The results of the studies on the relation between the number of pores and the current density with various admixtures is presented in Figure 4.

As we see from Figure 4, the number of pores in relation to the current density passes through a minimum in the presence of organic admixtures of surface tension lowering substances. The minimum porosity with such admixtures as acetone, formaldehyde, 2, 6 -- and 2, 7 -- disulfononaphtalinic acid swings in the direction of lower current densities as compared with the minimum on the porosity curve for pure electrolyte.

From Figure 4 it is evident that the minimum number of pores in a deposit occurs during electrolytic deposition of nickel from a solution with an admixture of 2,6 -- and 2,7 -- disulfononaphtalinic acid, suggested by Kudryavtsev.

The shifting of the minimum on the curve "number of pores -- current density" when surface tension lowering substances are introduced into the electrolyte as compared with the minimum for pure electrolyte is caused by the fact that after the admixtures are introduced into the electrolyte, a compact and uniform deposit is obtained only with lower current densities. Loshkarev and his collaborators showed that when surface tension lowering substances are introduced into the electrolyte the current densities necessary for compact and uniform deposits are lowered.

Thus, the shifting of the minimum on the curve "number of pores -- current density" in the direction of low current densities is caused by the fact that only with low current density values can compact and uniform deposits be obtained.

The increase of the number of pores in relation to current density in the presence of certain admixtures (formaldehyde, acetone) is caused by the fact that these admixtures are intensively reduced on the separate sections of the cathode surface, provoking the formation of pores with an action similar to that of hydrogen when it separates intensively on the cathode.

CONCLUSIONS

(1) It has been established that the number of pores in an electrolytic deposit of nickel sharply diminishes with an increase in thickness up to a definite point. With subsequent increase in thickness there is little change in the number of pores.

(2) It has been shown that the curve, "number of pores -- current density", passes through a minimum.

(3) It has been established that in relation to the admixtures of surface tension substances employed, the number of pores may either increase or decrease as compared to the electrolyte without

any mixture.

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